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PROCESS RESEARCH OF NON-CZ SILICON MATERIAL

Quarterly Report for the Period April 1—June 30, 1984

By
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Work Performed Under Contract No. NAS-7-100-956616

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FLAT-PLATE SOLAR ARRAY PROJECT
PROCESS DEVELOPMENT AREA

PROCESS RESEARCH OF NON-CZ SILICON MATERIAL

QUARTERLY REPORT NO. 3
April 1, 1984 to June 30, 1984

Contract No. 956616

The JPL Flat-Plate Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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A. CONTRACT GOALS AND OBJECTIVES

The objective of this contract is to investigate high risk-high payoff research areas on advanced processing techniques for non-CZ silicon sheet material that indicate promise of improving cost effectiveness of photovoltaic module production. The specific goals are as follows:

1. Simultaneous Diffusion of Front and Back Junctions

In this part of the program, the simultaneous diffusion of liquid boron and liquid phosphorus metallorganic precursors* into N-type dendritic silicon web is being investigated. The diffusion parameters required to achieve the desired P^+NN^+ cell structure will be determined, and the resultant cell properties will be compared to cells produced in a sequential diffusion process.

In addition to a standard tube diffusion furnace, a series of experiments will be carried out in a belt furnace. The parameters of cells produced with belt furnace diffusion will be compared with the parameters of baseline diffused cells.

2. Process Control Parameters and Sensitivities

During the program, the control parameters of the process will be analyzed; and the sensitivity of cell parameters to variations in these control parameters will be determined. Process control parameters to be studied are diffusion time and temperature; ambient gasses and flow rates; liquid diffusant source thickness and pre-bake conditions; and initial silicon material base resistivity.

3. Cost Analysis

A cost analysis will be performed on the simultaneous junction formation process using SAMICS-IPEG methodology. The results will be compared to a sequential diffusion process.

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*For brevity, these liquids will be referred to as liquid phosphorus and liquid boron dopants.

B. SUMMARY

This report describes work performed on JPL Contract 956616, "Process Research on Non-CZ Silicon Material" during April 1 through June 30, 1984. The program is designed to investigate the fabrication of solar cells on N-type base material by a simultaneous diffusion of N-type and P-type dopants to form an P^+NN^+ structure. The results of simultaneous diffusion experiments are being compared to cells fabricated using sequential diffusion of dopants into N-base material in the same resistivity range.

The process used for the fabrication of the simultaneously diffused P^+NN^+ cells follows the standard Westinghouse baseline sequence for P-base material except that the two diffusion processes (boron and phosphorus) are replaced by a single diffusion step.

All experiments are carried out on N-type dendritic web grown in the Westinghouse pre-pilot facility. The resistivities vary from 0.5 Ωcm to 5 Ωcm.

The dopant sources used for both the simultaneous and sequential diffusion experiments are commercial metallorganic solutions with phosphorus or boron components*. After these liquids are applied to the web surface, they are baked to form a hard glass which acts as a diffusion source at elevated temperatures.

In experiments performed thus far, cells produced in sequential diffusion tests have properties essentially equal to the baseline N^+PP^+ cells. However, the simultaneous diffusions have produced cells with much lower IV characteristics mainly due to cross-doping of the sources at the diffusion temperature.

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*These sources have been obtained from the following vendors:

- Allied Chemical Co.
- Diffusion Technology, Inc.

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This cross-doping is due to the high vapor pressure phosphorus (applied as a metallorganic to the back surface) diffusing through the SiO_2 mask and then acting as a diffusant source for the front surface.

C. TECHNICAL PROGRESS

1. Simultaneous Diffusion

The process sequence used in the diffusion experiments conducted in this program is shown in Table 1.

During the first six months of the contract, diffusion parameters were investigated to achieve the proper front and back junction depths.

Diffusion times from 18-25 minutes at 940°C-960°C in 1000 cc/min of N_2 produced P^+N junction depths from 0.2-0.3 μm and N^+N junction depths of 0.4-0.8 μm. Spreading resistance curves (Figures 1 and 2 of 2nd Quarterly Report) were obtained to determine the junction depth and junction gradient.

As has been reported previously, these experiments produced cells with generally low efficiency (1-4%) with an occasional 11% cell.

Using various diagnostic techniques, it was determined that the cells had a low shunt resistance (generally less than 100 Ωcm^2) and small areas of N-type material on the P^+ diffused surface. That is, the P^+ surface was being contaminated with the N-type diffusant (phosphorus).

A tentative model explaining the results of the simultaneous diffusion experiments is that the phosphorus species diffuse both into the silicon forming the N^+N back junction and outward through the glass diffusion mask. These phosphorus species then migrate as a gas or along the surface of the web and diffuse into the front surface of the cell. This excess phosphorus concentration at the surface and into the silicon prevents the boron from compensating the web and forming the P^+N junction.

Various glasses were tested for use as diffusion masks with the same results as given above; that is, front surface contamination.

TABLE 1

PROCESS SEQUENCE FOR SIMULTANEOUS DIFFUSION OF N-TYPE WEB

1. Pre-diffusion clean web strips per baseline sequence.

2. Using a P-type liquid metallorganic precursor, paint dopant on defined sunside of the web.

3. Dry and bake per vendor instructions.

4. Using a N-type liquid metallorganic precursor, paint dopant on backside of web.

5. Dry and bake per vendor instructions.

6. Diffuse at predetermined temperature, time, and gas ambients. (Optimum temperature, time, and gas ambients to be determined.)

An SiO_2 precursor recently became available which required baking at higher temperature (400°C for 30-40 minutes) but which was reported to form an impervious glass*. Experiments with this material consisted of coating the two sides of the cell blank with the boron and phosphorus dopants and baking to remove the excess solvent. The NP-5R SiO_2 solution was then applied with a sponge-squeegee and baked at 400°C for 40 minutes. The first two experiments in this series showed the contamination effect noted previously.

In a further experiment, a second layer of NP-5R was applied over the first in an attempt to increase the thickness and make the overall mask more impervious to out-diffusion of the phosphorus. However, the cells produced in this test exhibited the same contamination effect (i.e., low shunt resistances and low efficiencies).

A second method of applying the diffusion mask was also studied. In this technique, the web strip, coated with the baked P-type and N-type dopants, was dipped into the SiO_2 solution and slowly withdrawn. This method is completely analogous to the baseline sequence method for applying the antireflective coating. To achieve the proper mask thickness (1500-2000 Å), it was necessary to pull the web from the solution at about 30 cm/min. After baking to remove the solvent, the oxide layers covering the dopants appeared to be uniform, free of cracks and crystallization, and should form an impermeable diffusion mask.

In the first test, U1A (Diffusion Technology) SiO_2 was used. The data on this run is shown in Table 2. The cell efficiencies were very low. Several cells were stripped of metal and antireflective coating and the surfaces carefully mapped with a conductivity probe. On each cell blank, small areas of N-type conductivity were found on the P^+ side front surface. These small areas were apparently sufficient to short out the junction causing the low efficiency. The sheet resistivity was quite variable with values between 5 $\Omega/\square$ and 300 $\Omega/\square$. This is a further indication that phosphorus penetrated the front junction since values of 30-50 $\Omega/\square$ are normally obtained.

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*NP-5R from Allied Chemical Corporation

TABLE 2

SIMULTANEOUS DIFFUSION EXPERIMENTS CONDUCTED WITH DIFFUSION MASKS APPLIED BY DIP COATING

Run No.	P^+ Dopant	N^+ Dopant	Diffusion Conditions	Sheet Resistivity (Ω/□) N^+	Sheet Resistivity (Ω/□) P^+	Cell Efficiency	Mask
47520	B60	PX10	950°C/20 min 1800 cc/min N_2	7-9	Variable (5-300)	1-2%	U1A (Dipped) (2000 Å Thick)
50845	B60	PX10	950°C/20 min 1800 cc/min N_2	10-20	50-200	1-2%	NP-5R (Dipped) (1500 Å Thick)
50846	B60	PX10	950°C/20 min 1800 cc/min N_2	5-20	50-200	1-3%	NP-5R (Dipped) (2000 Å Thick)

Essentially similar results were obtained on the last two experiments indicating that the SiO_2 glasses were not adequate diffusion masks.

Based on the data from experiments in the first part of this program, it has become obvious that the diffusion masks being used are not capable of preventing the out-diffusion of phosphorus and subsequent contamination of the P^+ surface. The problem may be due to the material being used, its method of application, the method of forming the glass, the method of use, or some combination of the above. In any case, new approaches are mandatory to achieve simultaneously diffused junctions without cross-doping.

These new approaches and some initial results are given in the following section.

2. New Approaches to Simultaneous Junction Formation

a. Lower Temperature Diffusion

The phase diagram* of the SiO_2-P_2O_5 system shows that P_2O_5 forms a liquid in SiO_2 at temperatures slightly below 1000°C. This suggests the possibility that at 960°C the phosphorus has sufficient mobility to out-diffuse through the mask and onto the front surface. Accordingly, experiments were conducted in which the diffusion temperature was reduced by about 100°C to reduce the phosphorus mobility.

The first experiment was conducted using a diffusion temperature of 860°C for 60 minutes. Theoretically, these conditions should produce a BSF of about 0.3 µm and a front junction of 0.15 µm - both significantly more shallow than desired. However, it was felt that the experiment would produce information regarding the mobility of phosphorus. It would also afford an opportunity to determine IV characteristics of a cell with shallow junctions.

A second experiment was then conducted with the diffusion temperature increased slightly to 870°C with the diffusion time held fixed at 60 minutes. In this

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*T. Y. Tein and F. A. Hummel, J. Am. Ceram. Soc., 4S [9] 424, 1962.

experiment, the diffusion mask thickness was increased from 1500 Å to 2000 Å to determine if the thicker mask was more impervious to the phosphorus.

After the diffusion step, cell processing was completed using the baseline sequence. The IV properties of the cells were essentially the same as in previous simultaneous diffusion experiments, i.e., low open circuit voltage and low efficiency. All cells had a low shunt resistance of less than 100 Ωcm^2.

To further analyze the cells, the contact metal and antireflection coating were removed from several cells in each run. The front surface of the cells was mapped with a conductivity probe showing small areas of N-type material which could act as a shunt leading to the low Voc and low efficiency.

It should be noted that the first low temperature experiment was conducted in a newly cleaned diffusion tube which was tested and found free of contamination. Since the cells produced from this run had similar front surface N-type areas as those in previous simultaneous junction experiments, it is concluded that the source of the noted contamination is not the diffusion tube.

Table 3 summarizes results of the low temperature diffusion experiments along with other experiments described below.

b. Arsenic Diffusion

Arsenic is a much slower diffuser than phosphorus. Therefore, a simultaneous diffusion can be carried out at 950°C-960°C which will give the required P^+N junction depth of 0.2-0.3 μm. At this temperature, the As doped back N^+N junction should be 0.3-0.4 μm deep.

For the first experiment with the new doping species, an arsenic doped liquid precursor, AS-120, was used. This material was obtained from Allied Chemical and is an arsenic compound in ethyl alcohol.

TABLE 3

SIMULTANEOUS DIFFUSION EXPERIMENT SUMMARY

Run ID	Dopants		Diffusion Conditions	Sheet Resistivity ($\Omega/\square$)		Cell Efficiency	Mask	Results
	N^+	P^+		N^+	P^+			
50849 (N-base web)	PX-10	B-60	860°C/60 min 1000 cc/min N_2	20-60	3-60	Low Voc <1%	500 Å - U1A Dipped 500°C Bake	Low Voc (<20 mV) precluded any efficiency meas.
50850 (N-base web)	PX-10	Dil. B-60 (50/50)	870°C/60 min 1000 cc/min N_2 200 cc/min O_2	20-200	30-300	<1%	2000 Å - U1A Dipped 400°C Bake	Voc slightly higher but poor cells
49252 (N-base web)	As-120	Dil. B-60 (50/50)	950°C/20 min 1000 cc/min N_2 180 cc/min O_2	50-200	Variable 45-250	Max. 3%	1500 Å - U1A Dipped 500°C bake	Max. Voc = 300 mV Some strips showed N^+ contamination.
49253 (P-base web)	PX-10	B-60	860°C/20 min 1000 cc/min N_2 180 cc/min O_2	60-100	100-300	Mx. 8%	1500 Å - U1A Dipped 400°C Bake	Av Voc = 480 mV Av Jsc = 26 mA/cm^2 Low FF Efficiency 5-8%

The arsenic dopant was applied in the same manner as the PX-10 used in the earlier experiments. After application, it was dried under a heat lamp at 90°C and then baked at 200°C in air for 20 minutes. The SiO_2 diffusion mask was applied over the baked dopant.

Row 3 in Table 3 gives data on the first arsenic experiment together with cell data after baseline processing.

The cells had low efficiencies, and most of the cells had open circuit voltages of less than 100 mV. However, a number of cells had an open circuit voltage above 300 mV and efficiencies of about 3%. All cells showed a low shunt resistance from 40 to 200 Ωcm^2.

Representative cells from this run were stripped of metal and AR coating. On these cells, only a few small areas of N^+ conductivity were found on the P^+ surface. Since this technique showed somewhat less contamination, further tests will be made.

c. Simultaneous Diffusion of P-Type Web

Throughout this program, emphasis has been placed on the simultaneous diffusion of N-type web. With N-type web, the back N^+N junction (doped with fast diffusing phosphorus) can be diffused deep into the web while achieving a shallow front P^+N junction (doped with slower diffusing boron).

Several experiments have recently been carried out with P-type web. To retain the shallow front junction (≈0.3 μm), the diffusion was carried out at ≈860°C and thus the back jucntion (boron doped) is extremely shallow resulting in a poorer back surface field. However, it has been postulated that by using lower resistivity material, reasonable cell performance could be achieved.

Row 4 of Table 3 gives data on one of these runs.

The P-base cells exhibited a low average Voc (480 mV) and Jsc (26 mA/cm^2). The fill factor varied from 0.40-0.60, and the efficiencies varied from 5% to 8%.

Dark IV data was obtained on two selected P-base, simultaneously diffused cells. Both cells had excellent shunt resistances - in excess of 100 kΩcm^2. However, the series resistance of the cells was 60 Ωcm^2 and 73 Ωcm^2 respectively. Such a large series resistance cannot be totally ohmic since it would reduce Jsc to nearly zero.

To determine if the large measured resistance might be due to a Schottkey barrier on the back surface, a portion of the back metallization was removed and a Ga-In contact applied. (The Ga-In eutectic alloy is known to make ohmic contact to high resistivity P-type material.) This treatment increased the Voc by 20 mV and increased the efficiency by 1%.

The same effect was noted when the back surface was damaged by sandblasting. The Voc of these cells also increased by 20-30 mV with about a 1% absolute efficiency increase.

These data show that at the 860°C diffusion temperature, the boron doped junction was quite shallow and the metallization formed a Schottkey barrier on the back surface. The barrier caused an anomolously high series resistance.

Further tests will be carried out in an attempt to improve the back metallization contact resistance.

3. Sequential Diffusion in N-Type Web

In previous reports, it was shown that the sequential diffusion of boron and phosphorus into N-type web produced cells with efficiencies equal to the baseline P-type web.

D. ACTIVITIES PLANNED FOR NEXT QUARTER

1. Continue experiments with As as the N^+ dopant.

2. Carry out simultaneous diffusion experiments on P-type web where the back surface will be damaged to assure ohmic contact.

E. PROGRAM DOCUMENTATION AND DELIVERABLES STATUS

All programmatic and technical documentation specified in the subject contract (956616) have been prepared and submitted in accordance with contract schedular requirements. Table 4 summarizes submittal status of all routine reports (financial and monthly/quarterly technical reports). Table 5 summarizes submittal status of contract required documentation. All milestones scheduled to date have been met as shown on the Program Milestone Chart, Figure 3.

TABLE 4

ROUTINE PROGRAM DOCUMENTATION SUBMITTAL STATUS

Item	Submittal Date
1. MONTHLY TECHNICAL REPORTS	
A. November 1983	December 12, 1983
B. January 1984	February 8, 1984
C. February 1984	March 15, 1984
D. April 1984	May 15, 1984
E. May 1984	June 15, 1984
2. FINANCIAL MANAGEMENT REPORTS	
A. November 1983	December 12, 1983
B. December 1983	January 20, 1984
C. January 1984	February 15, 1984
D. February 1984	March 21, 1984
E. March 1984	April 23, 1984
F. April 1984	May 18, 1984
G. May 1984	June 22, 1984
3. QUARTERLY PROGRESS REPORTS	
A. No. 1	January 15, 1984
B. No. 2	April 15, 1984
C. No. 3	July 15, 1984

TABLE 5

SUMMARY PROGRAM DOCUMENTATION STATUS

Initial Baseline Cost Estimate	November 17, 1983
Program Plan	November 17, 1983

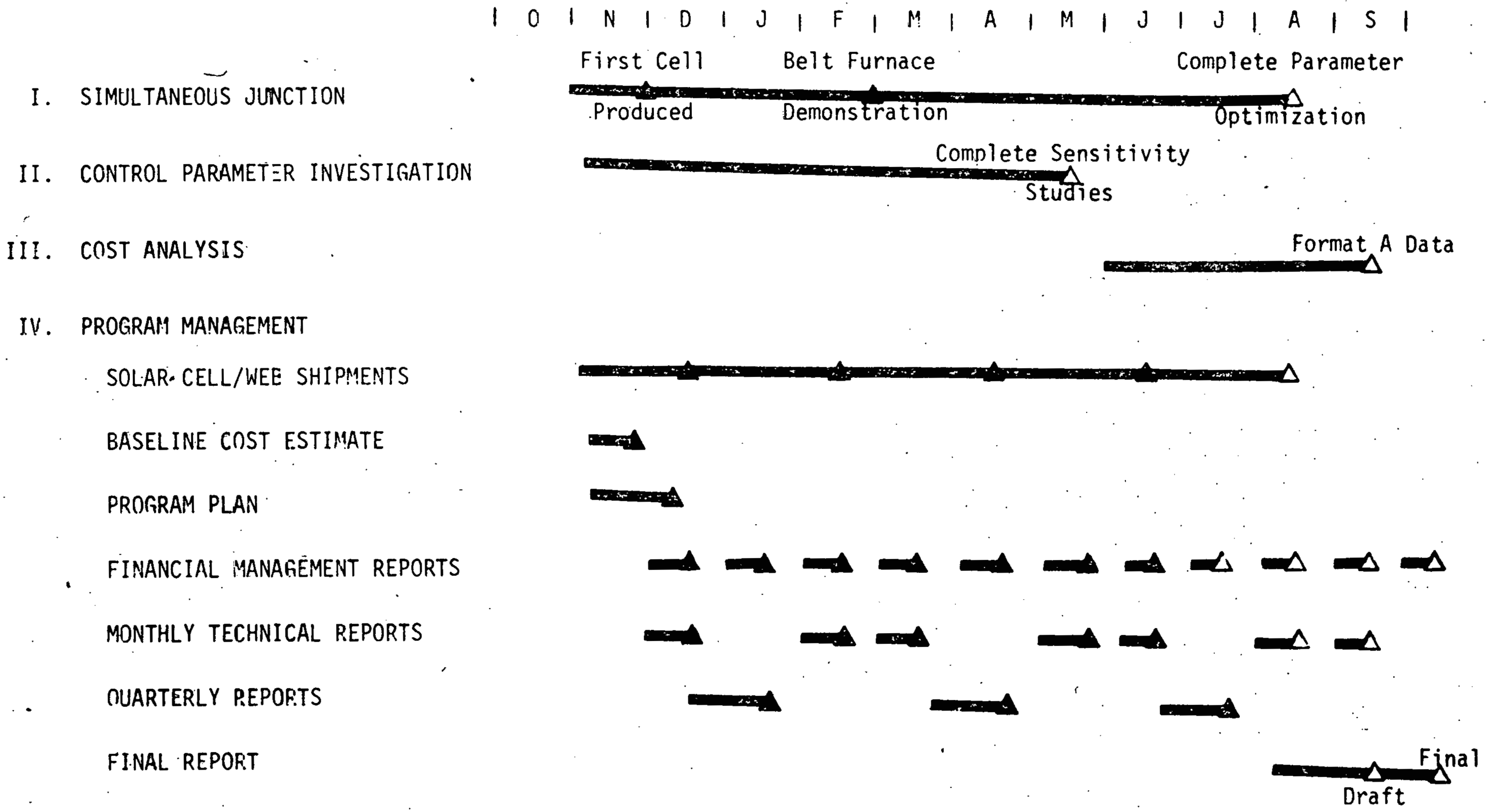

Figure 3. Process Research of Non-CZ Silicon Material Milestone Chart

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